Structural Studies of Some *o*- and *p*-Nitrophenylcarbamates by IR Spectroscopy and X-Ray Diffraction

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N-Alkyl-*o*-nitrophenylcarbamates as solids present two carbonyl stretching bands in the region 1700 – 1800 cm^{-1} but similar *N*-alkyl-*p*-nitrophenylcarbamates have only one such band in the IR spectrum. In solution both kinds of carbamate present one carbonyl stretching band, but for the former, the splittings occur when the carbamates crystallize. Four crystal structures were analyzed by X-ray diffraction. The two *ortho* derivatives have more than one molecule in the asymmetric unit, which is consistent with the IR observations.

Key words: *N*-*iso*-Propyl-*p*-nitrophenylcarbamate, *N*-*iso*-Propyl-*o*-nitrophenylcarbamate, *N*-Cyclohexyl-*o*-nitrophenylcarbamate, IR Spectroscopy, X-Ray Diffraction

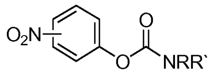
Introduction

Among carbamate derivatives there have been found many physiologically active compounds with applications in the pharmaceutical and agrochemical industries [1]. Various methods are available for the preparation of different kinds of carbamates [1, 2].

Bis(*o*-nitrophenyl)carbonate [3] is a new alternative starting material for obtaining carbamates [4]. It has the advantages of being less toxic than other reagents such as phosgene, diphosgene or carbon monoxide, more reactive than diethyl carbonate, *bis*(*p*-nitrophenyl)carbonate or urea, and readily soluble in a wide range of solvents.

A fast, high-yield synthesis of new *o*-nitrophenylcarbamates under mild conditions has recently been reported [4b]. During the characterization by IR spectroscopy of the crystalline *o*-nitrophenylcarbamates thus obtained, it was noticed that *N*-alkyl-*o*-nitrophenylcarbamates as solids present two absorption bands in the region 1700 – 1800 cm^{-1} [4b], but *N,N*-dialkyl-*o*-nitrophenylcarbamates only one. At first we tentatively attibuted this to the presence of hydrogen bonds N–H···O=C in the first case and their corresponding absence in the second, but when similar *N*-alkyl-*p*-nitrophenylcarbamates were analyzed by IR spectroscopy it was observed that they have only one carbonyl stretching vibration band [2f, 4b]. Our earlier studies showed that in solution both *o*- and *p*-nitrophenylcarbamates have a single carbonyl absorption band [4a]. This information is summarized in Table 1.

Table 1. The carbonyl stretching vibration bands of nitrophenylcarbamates [2f, 4].



	— -NO_2 position — — R (R′), $\nu_{C=O}$ (cm^{-1}) —			
Compound	*ortho*		*para*	
	Solid state [4b]	in CH_2Cl_2 [4a]	Solid state [4b] ([2f])	in CH_2Cl_2 [4a]
iso-Propyl(H)	1748, 1707	–	1712 (1730)	–
n-Propyl(H)	1750, 1715	–	1709 (1725)	–
n-Butyl(H)	1742, 1715	1757	–	1752
iso-Butyl(H)	1747, 1714	1757	–	1754
sec-Butyl(H)	1747, 1711	1754	–	1751
tert-Butyl(H)	–	1761	–	1757
c-C_6H_{11}(H)	1749, 1717	–	(1730)	–
$CH_2C_6H_5$(H)	1728, 1709	–	–	–
c-C_6H_{11}-(*c*-C_6H_{11})	1720	–	–	–
$CH_2C_6H_5$-($CH_2C_6H_5$)	1711	–	–	–

We have studied the variations in the IR spectra that occur when carbamates crystallize from CH_2Cl_2 by

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evaporation. Furthermore, the crystal structures of four compounds were analyzed by X-ray diffraction.

Results and Discussion

Crystallization from dichloromethane of two *N*-alkyl-*o*-nitrophenylcarbamates and one *N*-alkyl-*p*-nitrophenylcarbamate was studied by IR spectroscopy using an ATR accessory. The modifications that occur in the IR spectra in the regions 1800 – 1600 cm^{-1} and 3500 – 3200 cm^{-1} were studied as the solvent evaporated (Fig. 1). As we expected, the crystallization is accompanied by a shift of the absorption band from a higher wavenumber, characterized by an assumed non-associated form in a non-polar solvent, to a lower wavenumber in the crystalline compound containing intermolecular hydrogen bonds.

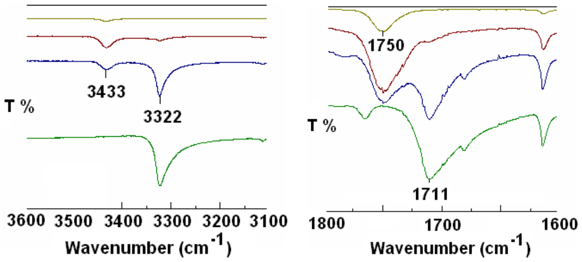

Fig. 1a. IR spectra of *N*-*iso*-propyl-*p*-nitrophenylcarbamate (left: 3600 – 3100 cm^{-1} region; right: 1800 – 1600 cm^{-1} region) at various concentrations in CH_2Cl_2 (top: dilute, bottom: solid state).

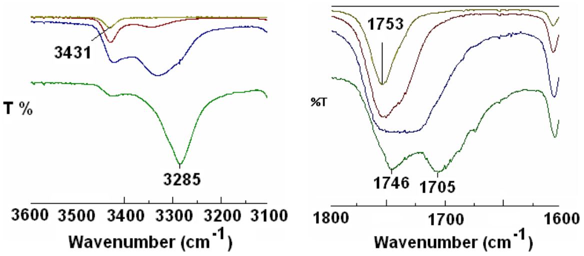

Fig. 1b. IR spectra of *N*-*iso*-propyl-*o*-nitrophenylcarbamate (left: 3600 – 3100 cm^{-1} region; right: 1800 – 1600 cm^{-1} region) at various concentrations in CH_2Cl_2 (top: dilute, bottom: solid state).

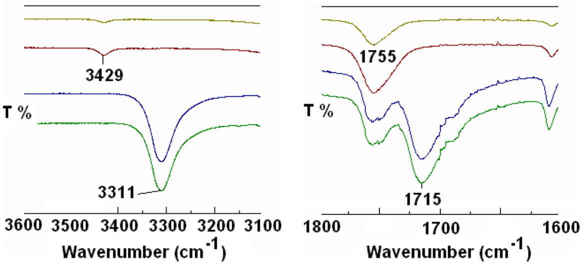

Fig. 1c. IR spectra of *N*-cyclohexyl-*o*-nitrophenylcarbamate (left: 3600 – 3100 cm^{-1} region; right: 1800 – 1600 cm^{-1} region) at various concentrations in CH_2Cl_2 (top: dilute, bottom: solid state).

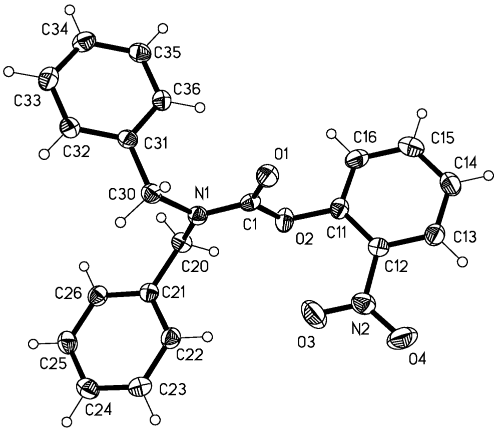

Fig. 2. The molecule of compound **4** in the crystal. Ellipsoids represent 50 % probability levels.

For *N*-*iso*-propyl-*p*-nitrophenylcarbamate (**1**) the NH vibration band appears in solution at 3433 cm^{-1} and in the solid state at 3322 cm^{-1}. The carbonyl group absorbs at 1750 cm^{-1} in CH_2Cl_2 but in the solid state at 1711 cm^{-1}.

N-*iso*-Propyl-*o*-nitrophenylcarbamate (**2**) has an NH vibration band in solution at 3431 cm^{-1} but in the solid state at 3285 cm^{-1}. Its carbonyl stretching band appears in CH_2Cl_2 at 1753 cm^{-1}, but during the concentration of the solution this band becomes broader and shifts to a lower wavenumber, finally splitting into two bands at 1746 and at 1705 cm^{-1}.

N-Cyclohexyl-*o*-nitrophenylcarbamate (**3**) displays a similar behavior to the other two carbamates in the region 3500 – 3200 cm^{-1}: in CH_2Cl_2 solutions the NH group absorbs at 3429 cm^{-1} but in the solid state at 3311 cm^{-1}. In the 1800 – 1600 cm^{-1} region the modifications are the following: in solution there is only one band at 1755 cm^{-1}, but during evaporation this band is shifted to 1753 cm^{-1}, and a new band appears and grows in intensity at 1715 cm^{-1}.

These results led us to believe that it is possible, as in crystalline forms of *o*-nitrophenylcarbamates, that the carbonyl group could exist in both associated and non-associated forms.

The crystal structures of the three compounds (**1** – **3**) and of *N*,*N*-dibenzyl-*o*-nitrophenylcarbamate (**4**) were analyzed by X-ray diffraction. The latter compound, which in contrast to the other compounds does not have

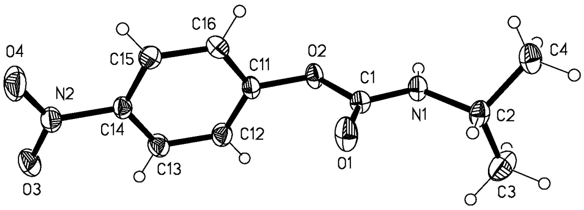

Fig. 3. The molecule of compound **1** in the crystal. Ellipsoids represent 50 % probability levels.

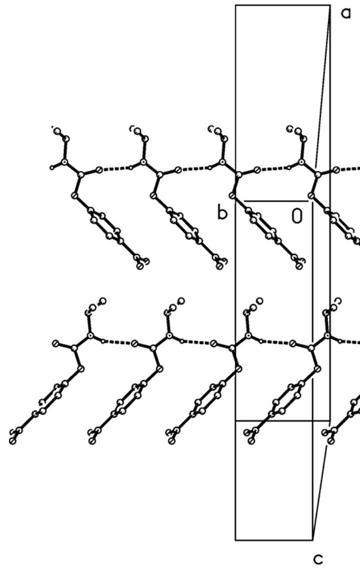

Fig. 4. Packing diagram of compound **1** viewed perpendicular to the *bc* plane in the region $x \approx 1/8$; there are similar layers at intervals of $x/4$. Classical hydrogen bonds are indicated by dashed lines.

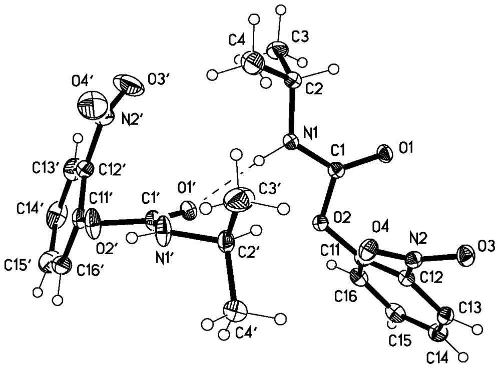

Fig. 5. The two independent molecules of compound **2** in the crystal. Ellipsoids represent 50 % probability levels. The dashed line indicates a hydrogen bond.

an NH group (Fig. 2), crystallizes as isolated molecules (neglecting "weak" hydrogen bonds of the form C–H···O).

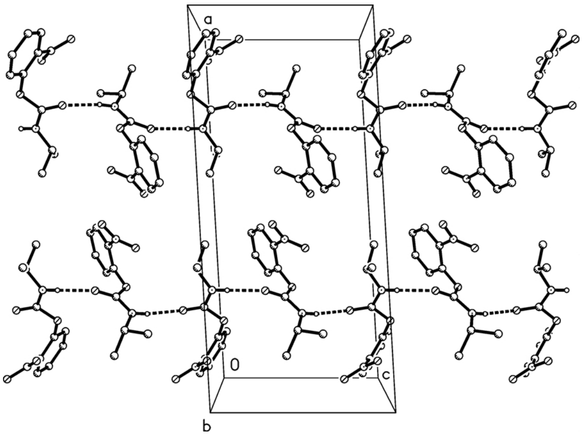

Fig. 6. Packing diagram of compound **2** viewed parallel to the *b* axis; there are two such layers in the cell. Classical hydrogen bonds are indicated by dashed lines.

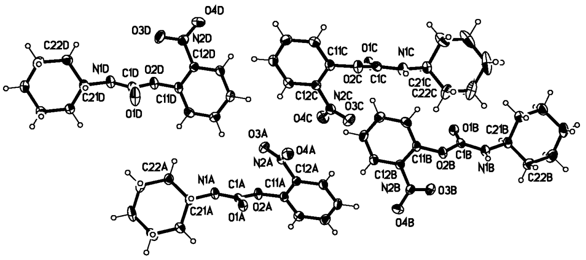

Fig. 7. The four independent molecules of compound **3** in the crystal. Ellipsoids represent 50 % probability levels.

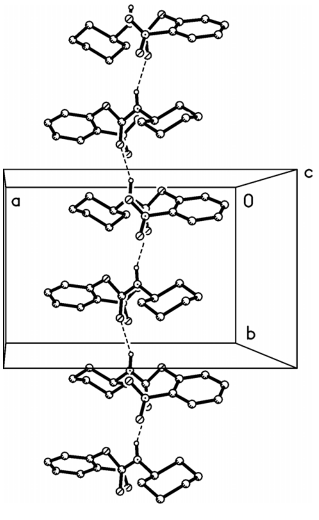

Fig. 8. Packing of the first independent molecule for compound **3**. Dashed lines represent hydrogen bonds.

In contrast, the molecules of the *N*-alkyl-nitrophenylcarbamates are linked by hydrogen bonds N–H···O=C, forming chains of molecules. *N*-*iso*-Prop-

Table 2. Classical hydrogen bonds (Å, deg) in compounds **1**–**3**[a].

Carbamate	D–H···A	D–H	H···A	D···A	D–H···A
1	N1–H1···O1$^{(i)}$	0.880(17)	2.031(17)	2.8721(16)	159.6(15)
2	N1–H1···O1$^{(i)}$	0.870(15)	2.045(16)	2.9076(14)	170.8(14)
	N1′–H1′···O1$^{(ii)}$	0.818(16)	2.029(17)	2.8463(15)	177.7(15)
3	N1A–H1A···O1A$^{(iii)}$	0.873(16)	2.023(17)	2.8553(19)	159.0(19)
	N1B–H1B···O1B$^{(iv)}$	0.855(16)	2.020(17)	2.867(2)	171.0(18)
	N1C–H1C···O1C$^{(v)}$	0.880(15)	1.958(16)	2.837(2)	176.7(19)
	N1D–H1D···O1D$^{(vi)}$	0.858(16)	2.013(16)	2.853(2)	166.2(19)

[a] Symmetry operators: (i) $x, -1+y, z$; (ii) $x, y, 1+z$; (iii) $1-x, -\frac{1}{2}+y, 1-z$; (iv) $2-x, \frac{1}{2}+y, -z$; (v) $1-x, \frac{1}{2}+y, -z$; (vi) $-x, -\frac{1}{2}+y, 1-z$.

Table 3. Crystal data and details of refinement.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{10}H_{12}N_2O_4$	$C_{10}H_{12}N_2O_4$	$C_{13}H_{16}N_2O_4$	$C_{21}H_{18}N_2O_4$
M_r	224.22	224.22	264.28	362.37
Crystal size, mm^3	0.23 × 0.23 × 0.1	0.4 × 0.2 × 0.08	0.45 × 0.16 × 0.08	0.4 × 0.2 × 0.14
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1$	$P2_1/c$
a, Å	21.429(5)	19.704(2)	13.6763(12)	11.3754(11)
b, Å	5.0431(11)	12.6758(12)	9.2727(8)	18.8820(16)
c, Å	22.145(5)	8.9795(8)	20.795(2)	8.4719(8)
β, deg	115.597(11)	93.221(4)	94.244(4)	104.611(4)
V, Å^3	2158.3(8)	2239.2(4)	2629.9(4)	1760.8(3)
Z	8	8	8	4
D_{calcd}, g cm^{-3}	1.380	1.330	1.335	1.367
$F(000)$	944	944	1120	760
μ, mm^{-1}	0.11	0.10	0.10	0.10
$2\theta_{\text{max}}$, deg	60	56.6	60	60
Total refl.	11715	22691	30602	20205
Indep. refl.	3158	5536	8119	5143
R(int)	0.127	0.038	0.037	0.127
Parameters	151	301	701	151
$wR2$ (all refl.)	0.139	0.101	0.083	0.109
$R1$ [$F \geq 4\sigma(F)$]	0.056	0.037	0.034	0.041
S	1.00	1.01	0.98	1.05
Max. $\Delta\rho$, e Å^{-3}	0.34	0.28	0.26	0.29

yl-*p*-nitrophenylcarbamate (**1**, Figs. 3 and 4) forms only one such chain, generated by translation parallel to the *b* axis. For the *N*-alkyl-*o*-nitrophenylcarbamates **2** and **3**, some unusual features were noticed: each of them presents more than one independent molecule in the asymmetric unit (two for *N*-*iso*-propyl-*o*-nitrophenylcarbamate (**2**), Figs. 5 and 6, and four for *N*-cyclohexyl-*o*-nitrophenylcarbamate (**3**), Figs. 7 and 8). The N–H···O=C chains in **2** involve translation parallel to the *c* axis, and the two independent molecules alternate in the chains. In **3**, each independent molecule makes its own chain parallel to the *b* axis *via* the 2_1 operator. Thus no non-associated carbonyl groups are observed for compounds **2**–**3** in the solid state. The presence in the asymmetric unit of more than one independent molecule, differing in conformation (see below), is the most probable reason for the presence of two carbonyl stretching bands in the IR spectra.

Bond lengths and angles may be considered normal. Torsion angles about the central N–C–O moieties are antiperiplanar (absolute values range from 169–179°), although the terminal substituents display slightly different torsion angles. A least-squares fit for the two independent molecules of **2** gave an r. m. s. deviation of only 0.22 Å for all non-H atoms, showing that the differences are not great. For compound **3**, orientations of the phenyl and cyclohexyl groups vary by up to 23° and 17°, respectively.

The geometry of the hydrogen bonds is shown in Table 2 and the crystal data in Table 3.

Conclusion

It has been demonstrated that the IR spectra of *N*-alkyl-*o*-nitrophenylcarbamates display one carbonyl stretching band in solution, but, upon evaporation of the solvents, an additional lower energy band appears.

The crystal structures of the carbamates revealed the existence of chains of N–H···O=C hydrogen bonded molecules. The observation of two carbonyl stretching bands in the IR spectra of the solid *o*-nitrophenylcarbamates is probably associated with the presence of more than one molecule in the asymmetric unit.

Experimental Section

IR spectra

IR spectra were recorded with a Jasco FT/IR-430 instrument using a Pike Technologies horizontal ATR accessory with a ZnSe crystal.

2.5 mL of a 0.03 M solution of carbamate in CH_2Cl_2 was prepared and placed on the ATR trapezoid, which is 80 mm long, 10 mm wide and 4 mm thick. This solution was used to record the first IR spectrum, and then the solvent was partially evaporated, and a second spectrum was recorded for the concentrated solution. The evaporation of the solvent was continued to dryness, whereupon the spectrum of the solid residue was recorded.

Crystal structure determinations by X-ray diffraction

N-*iso*-Propyl-*p*-nitrophenylcarbamate and *N,N*-dibenzyl-*o*-nitrophenylcarbamate were recrystallized from CH_2Cl_2-hexane, *N*-*iso*-propyl-*o*-nitrophenylcarbamate from CH_2Cl_2-heptane and *N*-cyclohexyl-*o*-nitrophenylcarbamate from toluene.

Data were measured at −140 °C using monochromated MoK_α radiation (λ = 0.71073 Å) on a Bruker SMART 1000 diffractometer. Structures were refined on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms bonded to nitrogen were refined freely; other hydrogens were included using a riding model or rigid methyl groups. For compound **3**, which crystallizes in a non-centrosymmetric space group, the anomalous dispersion effects were negligible and Friedel opposite reflections were therefore merged.

CCDC 694742-5 contain the supplementary crystallographic data for compounds **1**–**4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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